Gas-Phase Negative Ion Chemistry of Methyl Isocyanide

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Abstract: The gas-phase negative ion chemistry of methyl isocyanide (CH_3NC) has been studied at 0.4 Torr in a flowing afterglow apparatus and compared with that of its isomer acetonitrile (CH_3CN). Methyl isocyanide has been determined to be 1.8 ± 0.4 kcal/mol less acidic than acetonitrile in the gas phase, yielding $\Delta H^\circ_{acid}(CH_3NC) = 374 \pm 3$ kcal/mol. The isocyano group has been found to stabilize an adjacent radical site better than does the cyano group. Methyl isocyanide reacts with bases by competing proton abstraction and S_N2 processes. The reaction of the isocyanomethyl anion with a number of neutral reagents has also been studied. It undergoes hydrogen-deuterium exchange with D_2O while cyanide ion is a major product upon reaction with O_2, SO_2, N_2O, COS, CS_2, and C_6H_5CHO. Other ions are also produced in smaller amounts with many of these reagents. The rates of reaction of the isomeric anions with CH_3Br have also been determined.

Methyl isocyanide has long been of interest to organic chemists as a valuable synthetic intermediate,[1] and to physical chemists because its rearrangement to acetonitrile is a prototypical unimolecular reaction which can be treated theoretically with some success.[2] While this isomerization is 23.7 kcal/mol exothermic, there exists a substantial activation barrier (38.4 kcal/mol) for the interconversion.[3] Both the nitrile and the isocyanide contain a methyl group with relatively acidic hydrogens; proton abstraction from either gives distinct, synthetically useful anions that undergo nucleophilic reactions without isomerization.[1] Some positive ion reactions of methyl isocyanide, including its proton affinity, have recently been investigated in the gas phase,[4] and studies of its dissociative electron attachment have been reported.[5] The photoelectron spectroscopy of the isocyanomethyl anion is reported in an accompanying paper.[6] In this paper we report the first studies of the gas-phase negative ion chemistry of CH_3NC and of its conjugate base $^-CH_2NC$ and compare the reactions of these species with those of their isomers CH_3CN and CH_2CN^-.[7] In addition, we have measured the gas-phase acidity of methyl isocyanide and bracketed the electron affinity of the corresponding radical $^\bullet CH_2NC$. Isocyanomethyl and cyanomethyl anions are shown to be distinct, non-interconverting chemical entities. However, the higher ground-state energy of the former ion, and of its neutral precursor, gives rise to some unique reactions not observed for the latter.

Experimental Section

Experiments were carried out at 298 K in a conventional flowing afterglow that has been described previously.[8] Dissociative electron attachment to CF_4 generates F^- and dissociative electron attachment to NH_3 generates NH_2^-; these ions were used to produce all other ions. Proton abstraction by NH_2^- from H_2O, CH_3NC, CH_3CN, or CF_3CH_2OH generates HO^-, $^-CH_2NC$, CH_2CN^-, or $CF_3CH_2O^-$, respectively; elimination[9] from 1,2-dimethoxyethane or diethyl ether by NH_2^- generates CH_3O^- or $CH_3CH_2O^-$, respectively. The reaction of NH_2^- with di-*tert*-butyl peroxide produces *tert*-butoxide ion. Neutral reagents were added sufficiently far downstream from the region of reactant ion formation to ensure the absence of unwanted precursor ions.

Table I. Rate Constants for Proton Transfer between *tert*-Butoxide and Isocyanomethide

reaction	k_{obsd}[a]	k_{ADO}[a,b]
$(CH_3)_3CO^- + CH_3NC$	5.2×10^{-10}	2.7×10^{-9}
$^-CH_2NC + (CH_3)_3COH$	2.2×10^{-9}	2.1×10^{-9}

[a] Units of cm^3 molecule^{-1} s^{-1}. [b] Calculated by the method of ref 16.

All reactions were carried out at a helium pressure of 0.4 Torr. Rate constants were determined by monitoring reactant ion intensity as a function of reaction distance at known neutral reagent flow rates. Reported values are averages of three determinations and are estimated to be accurate to within ±20%. Branching ratios were found by plotting normalized product ion intensities vs. the change in reactant ion intensity and extrapolating to zero change in reactant ion intensity (zero neutral reagent flow), thereby eliminating contributions from secondary reactions.

Gases were obtained from commercial sources and were of the following purities: He (99.995%), NH_3 (99.999%), N_2O (99.99%), O_2 (99.95%), CO_2 (99.5%), SO_2 (99.9%), and COS (97.7%). Methyl isocyanide was prepared according to the literature procedure[10] and purified by several trap-to-trap distillations. Because of its high vapor pressure, methyl isocyanide was kept at 0 °C as it evaporated into the flow tube. Other reagents were obtained from commercial suppliers and used without further purification.

Results

Gas-Phase Acidity of CH_3NC. The gas-phase acidity of CH_3NC was measured by two methods. In the first, the forward and reverse rate constants for reaction 1 were determined (see Table I). The ratio of these rate constants gives the equilibrium

$$(CH_3)_3CO^- + CH_3NC \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CH_3)_3COH + {}^-CH_2NC \quad (1)$$

constant for proton transfer between *tert*-butyl alcohol and methyl isocyanide. The resulting ΔG° represents the difference in ΔG°_{acid} for these compounds; this value closely approximates the difference in ΔH°_{acid} since ΔS°_{acid} values are expected to be similar.[11] With use of the literature value for the gas-phase acidity of *tert*-butyl alcohol [$\Delta H^\circ_{acid}((CH_3)_3COH) = 373.3$ kcal/mol],[12] the gas-phase acidity of methyl isocyanide was calculated [$\Delta H^\circ_{acid}(CH_3NC) = 374.2$ kcal/mol]. For the forward rate measurement, *tert*-butoxide was formed in the absence of *tert*-butyl alcohol (see

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[6] Moran, S.; Ellis, H. B., Jr.; DeFrees, D. J.; Paulson, S. E.; Ellison, G. B. *J. Am. Chem. Soc.*, following paper in this issue.

[7] Photoelectron spectroscopy has shown that in the isocyanomethyl anion the negative charge is primarily located on the CH_2 group while in the cyanomethyl anion it is primarily on the nitrogen atom (ref 6). We have written the structures to reflect these conclusions.

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Table II. Product Ion Distribution and Reaction Enthalpies for the Reaction of Anions with Methyl Isocyanide and Acetonitrile

anion	neutral reactant	% S_N2	% PT	ΔH_{S_N2}[a]	ΔH_{PT}[a,b]
NH_2^-	CH_3NC	0	100	-57	-30
	CH_3CN	0	100	-34	-32
HO^-	CH_3NC	33	67	-40	-17
	CH_3CN	0	100	-17	-19
CH_3O^-	CH_3NC	10	90	-34	-5
	CH_3CN	0	100	-11	-7
$CH_3CH_2O^-$	CH_3NC	2	98	-31	-2
	CH_3CN	0	100	-7	-4
F^-	CH_3NC	100	0	-21	+3
	CH_3CN	0	100[c]	+2	+1
$CF_3CH_2O^-$	CH_3NC	no reaction		-18	+10
	CH_3CN.	no reaction		+6	+8

[a] kcal/mol. [b] Reference 15. [c] Proton transfer is the only reaction channel observed; due to the small endothermicity, the reaction efficiency is less than one.

Table III. Product Ion Distribution for Reactions of Isocyanomethide and Cyanomethide Ions

M	products	% from $^-CH_2NC$	% from CH_2CN^-
O_2	CN^-	95	0
	NCO^-[a]	5	0
SO_2	CN^-	61	0
	NCO^-	26	0
	SO_2^-	11	0
	adduct	2	100
N_2O	CN^-	50	0
	$CNCN_2^-$	50	100[b]
COS	CN^-	53	0
	$CNCH_2S^-$	20	3[b]
	C_2HSO^-	9	0
	HS^-	9	28
	Adduct	9	65
	$NCCCO^-$	0	4
CS_2	CN^-	75	0
	$C_2HS_2^-$	10	0
	$CNCCS^-$	6	63[b]
	NCS^-	5	0
	Adduct	4	31
	HS^-	0	6
C_6H_5CHO	CN^-	67	0
	NCO^-	33	0
	Adduct	0	100

[a] It is impossible, of course, to distinguish isocyano-containing ions from cyano-containing ions by the mass alone. Experiments indicate that cyanate (NCO^-), rather than its isomer fulminate (CNO^-), is formed in this reaction on the basis of its basicity. [b] Presumably the product ion formed by reaction of CH_2CN^- is an isomer of the product shown for reaction of $^-CH_2NC$.

Experimental Section). For the reverse rate measurement, $^-CH_2NC$ was formed by proton abstraction from CH_3NC. The presence of CH_3NC in the flow tube allows the forward reaction to proceed and can result in the measurement of an incorrectly small value for k_r. To minimize this effect, k_r was measured at early reaction times. The resulting value of k_r is about equal to the ADO[13] rate constant for this reaction, which corresponds to reaction at every collision and is, therefore, unlikely to be any larger.

The second determination of acidity involved measuring the equilibrium constant for reaction 2. This was accomplished by

$$^-CH_2NC + CD_3CN \rightleftarrows CH_2DNC + CD_2CN^- \qquad (2)$$

multiplying the ratio of the measured flow rates of the neutral reagents by the ratio of the measured ion intensities. Flow rates were increased until no change in the calculated equilibrium constant was found, assuring that equilibrium was achieved. $\Delta G°$ for the reaction was found to be 1.8 ± 0.4 kcal/mol. Assuming $\Delta G° \simeq \Delta H°$ for eq 2 and using $\Delta H°_{acid}(CH_3CN) = 372.2$ kcal/mol[12] gives $\Delta H°_{acid}(CH_3NC) = 374.0$ kcal/mol, in excellent agreement with the value obtained above. The acidities of *tert*-butyl alcohol and acetonitrile are known to an accuracy of ±2 kcal/mol; therefore, we report the gas-phase acidity of methyl isocyanide as 374 kcal/mol with a total propagated error of ±3 kcal/mol.

Electron Affinity of $^\bullet CH_2NC$. It is possible to bracket the electron affinity of a molecule by observing the occurrence or non-occurrence of charge transfer from its corresponding anion to a molecule of known electron affinity. Reaction 3 is not observed, but reaction 4 proceeds readily with 11% of the reaction occurring by electron transfer. The electron affinities of O_2 and

$$^-CH_2NC + O_2 \rightarrow {}^\bullet CH_2NC + O_2^- \qquad (3)$$

$$^-CH_2NC + SO_2 \rightarrow {}^\bullet CH_2NC + SO_2^- \qquad (4)$$

SO_2 are 0.440 ± 0.008 eV[14] and 1.097 ± 0.036 eV,[15,16] respectively. Thus from these results we assign EA($^\bullet CH_2NC$) = 0.8 ± 0.4 eV.[17] We have not attempted to increase the precision of this measurement because a very precise value (EA = 1.059 ± 0.024 eV) has been obtained by photoelectron spectroscopy; these results are reported in the accompanying papers.[6] We will use this value in subsequent discussions.

Reactions of Anions with CH_3NC and CH_3CN. The reactions of NH_2^-, HO^-, CH_3O^-, $CH_3CH_2O^-$, F^-, and $CF_3CH_2O^-$ with methyl isocyanide and acetonitrile were studied and the results are summarized in Table II. Acetonitrile reacts by proton abstraction if the anion is more basic than the cyanomethide anion and does not react otherwise. Methyl isocyanide, by contrast, can react both by proton transfer and by nucleophilic substitution to form CN^-. For example, it reacts with hydroxide ion as shown in eq 5. If the base is sufficiently strong (NH_2^-), only proton

$$\begin{aligned} HO^- + CH_3NC &\xrightarrow{67\%} {}^-CH_2NC + H_2O \\ &\xrightarrow{33\%} CN^- + CH_3OH \end{aligned} \qquad (5)$$

abstraction is observed. For bases weaker than hydroxide ion but still strong enough to abstract a proton (CH_3O^-, $CH_3CH_2O^-$) only a small amount of cyanide ion is observed (vide infra). Fluoride ion is insufficiently basic to abstract a proton from methyl isocyanide; it reacts only by S_N2 displacement to form CN^- ($k = 3.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). Trifluoroethoxide ion ($CF_3CH_2O^-$) does not react with either neutral reagent.

Reactions of $^-CH_2NC$ and CH_2CN^- with Neutral Molecules. The reactions of $^-CH_2NC$ and CH_2CN^- were studied with a variety of neutral molecules. Neither appears to react with NH_3 or H_2O, but both readily exchange two hydrogens with D_2O. The anion from acetonitrile exchanges two hydrogens with CH_3OD and with CH_3CH_2OD, while that from methyl isocyanide reacts by competitive exchange and production of CN^-. Both anions react with CF_3CH_2OD exclusively by rapid proton transfer to form $CF_3CH_2O^-$.

Finally, the reactions of the two anions with a variety of molecules not possessing acidic hydrogens are summarized in Table III.

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(17) While it is recognized that the non-occurrence of reaction 3 does not mean it is endothermic, $^-CH_2NC$ reacts with O_2 only very slowly ($k \cong 4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) by other pathways (see Table III). Charge transfer, if exothermic, is expected to occur relatively rapidly, since it has been observed for other carbanions. For example, allyl anion electron transfers to O_2 with $k = 2.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 3301–3309).

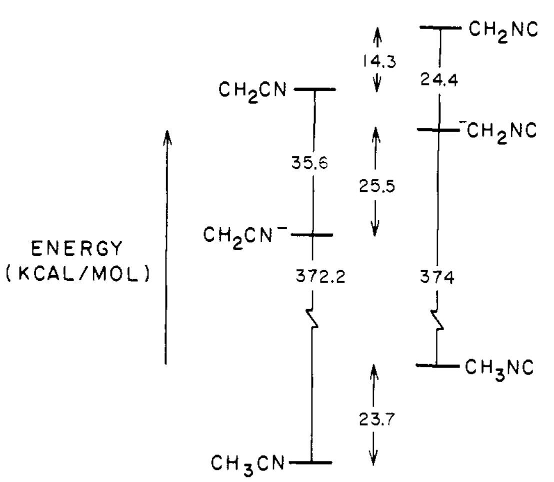

Figure 1. Relative energies of the cyano and isocyano parent compounds, their carbanions, and radicals.

Discussion

Acidity of CH_3NC and Electron Affinity of $^{\bullet}CH_2NC$. Methyl isocyanide (ΔH°_{acid} = 374 ± 3 kcal/mol) is only slightly less acidic in the gas phase than is acetonitrile (ΔH°_{acid} = 372.2 ± 2 kcal/mol). The acidity of an isocyanide does not seem to have been determined in solution, but acetonitrile has been determined to have pK_a = 31.3 in dimethyl sulfoxide solution.[18] There is chemical evidence that an isocyano group is less effective than a cyano group in stabilizing an adjacent carbanion. Schüllkopf,[1] for example, has noted that more strongly basic conditions are required to form the anion from methyl isocyanide than from acetonitrile. Stirling[19] has recently studied base-induced eliminations from $NCCH_2CH_2OTs$ and $CNCH_2CH_2OTs$ and found the former to be more rapid by a factor of 3.8×10^4, another manifestation of a greater acidifying effect of the cyano as compared to the isocyano group. Published high level ab initio calculations have given values, corrected for zero-point energy, of 372 and 381 kcal/mol for the gas-phase acidities of acetonitrile and methyl isocyanide, respectively.[20] Thus theory and experiment are in excellent agreement for the acidity of acetonitrile but differ by about 7 kcal/mol for the isocyanide. Calculations at still higher levels of theory,[6] far from closing this gap, widen it by 2 kcal/mol. This lack of agreement between theory and experiment, while still relatively small, is nevertheless surprising, and further studies are planned in the hope of resolving the discrepancy.

In contrast, the electron affinity of the isocyanomethyl radical (24.4 kcal/mol) is appreciably less than that of the cyanomethyl radical (35.6 kcal/mol). Figure 1 summarizes the relative energies of the two neutrals, radicals, and anions. From these data one can see that the isomerization energy from the isocyanide to the nitrile is approximately the same for the neutrals (23.7 kcal/mol) and the anions (25.5 kcal/mol) and appreciably less for the radicals (14.3 kcal/mol). Thus while the cyano and isocyano groups stabilize an adjacent carbanion to an approximately equal extent, the isocyano group is better than the cyano group at stabilizing an adjacent radical site. Calculations for the two radicals reproduce this difference satisfactorily.[21] It would be extremely interesting to know if there is a correspondingly lower activation energy for the isomerization of the radical as compared to the neutral or the anion.

Reactions of CH_3NC with Bases. In the reaction of a base with methyl isocyanide, two processes are in competition—proton abstraction and S_N2 displacement; acetonitrile undergoes only proton abstraction. For the oxyanions studied a consistent picture emerges; proton transfer is always an extremely fast reaction provided it is even slightly exothermic, while displacement is faster the stronger the base. For example, hydroxide ion is a very strong base (ΔH°_{acid} = 391 kcal/mol) and it reacts with methyl isocyanide to give a 2:1 mixture of proton abstraction and displacement (eq 5). The former reaction is 17 kcal/mol exothermic, the latter, 40 kcal/mol. Methoxide ion (ΔH°_{acid} = 379 kcal/mol), for which the corresponding exothermicities are 5 and 34 kcal/mol, respectively, gives 90% of the M − 1 ion and only 10% cyanide ion, and ethoxide ion (2 and 31 kcal/mol) gives 98% of the M − 1 ion. All of these reactions proceed, overall, at or near the collision rate. Thus, HO^-, CH_3O^-, and $CH_3CH_2O^-$ all abstract a proton readily from methyl isocyanide, but the S_N2 rate drops off for the less basic alkoxides, even though the exothermicity of the S_N2 reactions remains very high. Fluoride ion (ΔH°_{acid} = 371 kcal/mol) is not sufficiently basic to abstract a proton from methyl isocyanide, but it does induce displacement. The S_N2 reaction, which is exothermic by 21 kcal/mol, proceeds with a rate constant of 3.0×10^{-10} cm^3 molecule^{-1} s^{-1}. The isocyanide group is thus a poorer leaving group than chloride ion, since methyl chloride reacts six times more rapidly with fluoride ion in the gas phase.

Amide ion is an exception to this overall generalization in that, although it is an exceedingly strong base (ΔH°_{acid} = 403 kcal/mol), it gives only proton abstraction and no displacement with methyl isocyanide. It appears that amide ion is poorer as a nucleophile than would be expected, considering its great basicity. There are a few other indications in the literature that this is the case. For example, amide produces fluoride ion from methyl fluoride more slowly (1.8×10^{-11}) than does hydroxide ion (2.5×10^{-11}), and only slightly more rapidly than does methoxide ion (1.4×10^{-11}), in spite of the fact that amide ion is 12 kcal/mol stronger a base than the former and 24 kcal/mol than the latter.[22] Amide ion also reacts less rapidly (1.5×10^{-10}) with ethylene oxide than does hydroxide ion (2.5×10^{-10}).[23]

Reaction of $^-CH_2NC$ with Neutral Molecules. The isocyanomethyl anion reacts with a variety of neutral molecules, both those that contain relatively acidic protons and those that do not. It is convenient to consider these two types of reagents separately.

Neither cyano- nor isocyanomethyl anions appear to react with ammonia or water, but both readily exchange two protons with D_2O. No cyanide ion is formed in either case. The cyanomethyl anion also exchanges with CH_3OD and C_2H_5OD without further reaction. However, $^-CH_2NC$ reacts with CH_3OD and C_2H_5OD to give CN^- in competition with exchange. We picture these reactions to proceed as shown in eq 6. The isocyanomethyl anion

$$\begin{array}{l} {}^-CH_2NC + CH_3OD \rightleftarrows \\ \qquad [{}^-CH_2NC{\cdot}DOCH_3] \\ \qquad\qquad \uparrow\downarrow \\ \qquad [CH_2DNC{\cdot}{}^-OCH_3] \rightarrow CN^- + CH_2DOCH_3 \quad (6) \\ \qquad\qquad \uparrow\downarrow \\ \qquad [{}^-CHDNC{\cdot}HOCH_3] \rightarrow {}^-CHDNC + CH_3OH \end{array}$$

and CH_3OD are attracted to one another by ion–dipole and ion–induced dipole forces until they enter a relatively long-lived ion–dipole complex. This complex will contain 15–20 kcal/mol of energy arising from these attractive forces. A 5 kcal/mol endothermic deuteron transfer, using part of this energy, can produce a new complex, which will have insufficient energy to dissociate, but which will still have sufficient energy to surmount an S_N2 barrier to form cyanide ion. Some H–D exchange, resulting from proton abstraction and dissociation in competition with displacement, is also observed. A similar mechanistic scheme is used to account for H–D exchange by D_2O except that, in this case, the initial deuteron transfer is 17 kcal/mol endothermic, leading to a $[DO^-{\cdot}DCH_2NC]$ complex with insufficient energy to allow the corresponding S_N2 reaction to occur. In the latter example, we can effectively form the same complex in two different

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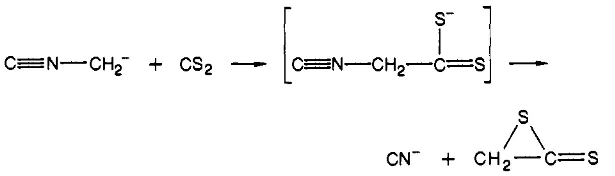
ways with differing amounts of energy. When it is formed in the exothermic direction from HO^- + CH_3NC, a large amount of CN^- is produced, since the initial complex has sufficient energy to traverse either the S_N2 or proton-transfer barrier. When the same complex is formed in the endothermic direction from $^-CH_2NC$ + D_2O, the resulting complex has insufficient energy to surmount the S_N2 barrier so that only proton transfer, and hence H–D exchange, is observed.

A number of molecules that do not possess acidic hydrogens nevertheless react with $^-CH_2NC$ to produce CN^- as well as other ionic products. The ionic products and branching ratios for the reactions of $^-CH_2NC$ and CH_2CN^- with O_2, SO_2, N_2O, COS, CS_2, and C_6H_5CHO are given in Table III. In every case, CN^- amounts to 50% or more of the product ions when $^-CH_2NC$ is the reactant ion whereas no CN^- is formed upon reaction with CH_2CN^-. Quite clearly, the higher internal energy of the former ion reveals itself in these reactions.

When $^-CH_2NC$ is allowed to react with COS or CS_2, cyanide ion is the major product in each case, comprising 53% and 75% of the ionic products, respectively. No cyanide ion is produced with either of these two reagents when they are allowed to react with CH_2CN^-; instead, the major product ions arise by addition or addition followed by loss of H_2S. These results suggest that CN^- is formed by addition followed by an internal S_N2 reaction (eq 7). Some evidence for this mechanism is provided by the appearance of ions of m/z 89 and 73, corresponding to $C_2HS_2^-$ and C_2HSO^-; these could arise by proton abstraction from the neutral product by CN^- produced in the reaction before it escapes from the product ion–dipole complex. These ions may be cyclic, or ring opening may occur as shown in eq 8.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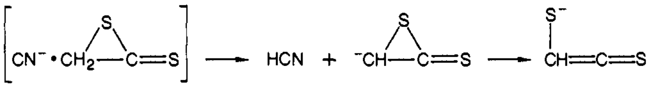
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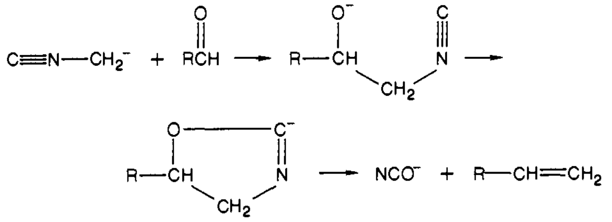
The other ions produced in these reactions with COS and CS_2 have precedent from earlier studies. Sulfur atom transfer with expulsion of CO is a common reaction of COS[24] and is observed for both $^-CH_2NC$ and CH_2CN^-. Sulfur atom transfer occurs less easily from CS_2 and is not observed from either of these weakly basic anions. We have also noted previously that addition reactions to CS_2 are more likely to lead to further fragmentation than are those of COS.[25] This trend is observed again here; with CH_2CN^- the major product with COS is addition, whereas with CS_2 it is addition and fragmentation with loss of H_2S.

The isocyanomethide ion reacts with benzaldehyde to give both CN^- and a Wittig-type olefination reaction to produce NCO^- (eq 9). This latter reaction has been observed in solution for the anion from methyl isocyanide, where the intermediate heterocyclic anion can be trapped and whose decomposition to olefin has been shown to be stereospecific in appropriate cases.[1a] Presumably CN^- results from displacement to form the epoxide. Cyanide ion is also formed upon reaction of $^-CH_2NC$ with O_2 and SO_2. With O_2, a trace of NCO^- is also produced and an even greater amount of NCO^- is produced by reaction with SO_2. The mechanism of formation of these ions is presumably analogous, namely addition followed by internal displacement of CN^- or cyclization and expulsion of NCO^- (eq 9).


(9)

In a previous paper we noted that CH_2CN^- does not react with O_2 but forms NCO^- upon reaction with $O_2(a^1\Delta_g)$.[26] At that time we proposed that reactions with ground-state $O_2(X^3\Sigma_g^-)$ are initiated by electron transfer from the anion to O_2 followed by peroxide formation. Such an endothermic electron transfer could occur from $^-CH_2NC$ to O_2 making use of the ion–dipole attractive energy, but there is insufficient energy in the complex to drive electron transfer from CH_2CN^- to O_2.

Finally, we have examined briefly the S_N2 reaction rates of the two isomeric anions with CH_3Br. Earlier studies of gas-phase S_N2 reactions have indicated that delocalized anions undergo S_N2 reactions more slowly than do localized anions of the same basicity.[27] These two anions are nearly the same base strength, yet the isocyanomethyl anion is proposed to be more pyramidal, less delocalized than the cyanomethide anion. We thought that this difference in structure might manifest itself in a large difference in S_N2 rates for the two anions. However, the rate constants are similar, with the slightly more basic anion $^-CH_2NC$ reacting slightly faster ($k = 8.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) than CH_2CN^- ($k = 5.1 \times 10^{-10}$).

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Registry No. CH_3NC, 593-75-9; $^{\cdot}CH_2NC$, 70971-59-4; $^-CH_2NC$, 81704-80-5.

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[26] Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H. *EHP, Environ. Health Perspect.* **1980**, *36*, 119–134.

[27] For example, the allyl anion reacts with methyl chloride at only 19% of the rate at which HO^- reacts, although the two anions are equally basic. See: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 901–902. Also see ref 22.